Ultra-Thin Electro-Spun PAN Nanofiber Membrane for High-Efficient Inhalable PM2.5 Particles Filtration

Article *in* Journal of Nano Research · March 2017

DOI: 10.4028/www.scientific.net/JNanoR.46.73

CITATIONS
0

READS
102

7 authors, including:

Shi Su
Southeast University (China)
19 PUBLICATIONS **119** CITATIONS
SEE PROFILE

Lei Zhou
The University of Warwick
7 PUBLICATIONS **19** CITATIONS
SEE PROFILE

Litao Sun
Southeast University (China)
194 PUBLICATIONS **5,396** CITATIONS
SEE PROFILE

Ultra-thin Electro-Spun PAN Nanofiber Membrane for High-Efficient Inhalable PM2.5 Particles Filtration

SHI SU[1], JIANGLING LI[2], LEI ZHOU[3], SHU WAN[1], HENGCHANG BI[4], QING MA[1], and LITAO SUN[1,a *]

[1]SEU-FEI Nano-Pico Center, Key Laboratory of MEMS of Ministry of Education, Collaborative Innovation Center for Micro/Nano Fabrication, Device and System, Southeast University, Nanjing 210096, P. R. China.

[2]Department Science and Engineering, Bournville College, Birmingham, B31 2AJ, United Kingdom.

[3]WMG, University of Warwick, United Kingdom.

[4]Center for Advanced Carbon Materials, Southeast University and Jiangnan Graphene Research Institute, Changzhou 213100, P. R. China.

[5]Southeast University-Monash University Joint Research Institute, Suzhou 215123, P. R. China.

* Corresponding Author: Email: slt@seu.edu.cn

Keywords: electrospun; nanofiber; inhalable particles; filtration.

Abstract. In this work, we introduce a synthesis method for a nanofiber membrane made of polyacrylonitrile and verify its filtration efficiency with micron-size particles. The polyacrylonitrile nanofiber membrane was produced by electro-spun technique with a thickness less than 0.2 mm. The filtration experimental result from micron-size particle penetration proved that after 60-min deposition, the polyacrylonitrile nanofiber membrane successfully filtrated ~99% micron-size particles in solution. We found that uniform morphology, consistent nanofiber diameter without disordered beads will lead to a better filtration performance. It also demonstrated a relatively stable chemical properties in acid solution, and this finding will provide a low-cost, environmental-friendly and straightforward filtration approach for future $PM_{2.5}$ elimination in an aqueous and harsh environment.

Introduction

The air pollution in China, especially inhalable particles with diameters less than 2.5 micron meters ($PM_{2.5}$), has attracted wide concern by Chinese citizens and the press [1]. Some evidence suggests that exposure to $PM_{2.5}$ can cause lung cancer and make pregnant women to have low weight babies [2]. Hence, long-time exposure in $PM_{2.5}$ atmosphere will potentially increase the possibility of lung morbidity as well as mortality. These $PM_{2.5}$ particles are mainly produced by industrial coal use and combustion of fossil fuel by transportation vehicles [3]. However, as no alternative energy source has been developed, it is difficult to reduce the $PM_{2.5}$ by simply cutting off the coal consumption [4]. A practical method is to filter the micro-particles via porous fibers before the combustion gases have been emitted to the air.

At this time, several electro-spun polymer nanofibers have been developed to filter the micron-size particles. Different approach of reducing $PM_{2.5}$ in public are commonly focused on outdoor elimination, such as mask filter, individual protection, as well as air exchange. Polyvinyl alcohol (PVA) and polyethylene oxide (PEO) have been used to produce the nanofibers for filtration applications [5],[6]. However, the PVA materials are soluble in water, which limits their use for large-scale applications in

open air. On the other hand, PEO is explosive and a biological hazard. Thus, it is not suitable for high-temperature applications and can lead to potential secondary pollution. Some research used polyactide (PLA) for electrospun deposition, but this is not stable enough in a high-temperature environment [7]. Industrial nanofibers used for applications in the real environment should be insoluble with a high melting point, biocompatible and convenient for mass-production. In addition, coal combustion always contains an emission of SO_2 and NO_x, which can be mixed with water in air and then oxidized to SO^{3-} and NO^{3-} [8]. Therefore, the nanofibers should also be chemically stable within an aqueous acid environment. Recent techniques on nanofibers have focused on applications of polyacrylonitrile (PAN) based materials with electrospun nanofibers because of their excellent mechanical and chemical stabilization properties [9],[10].

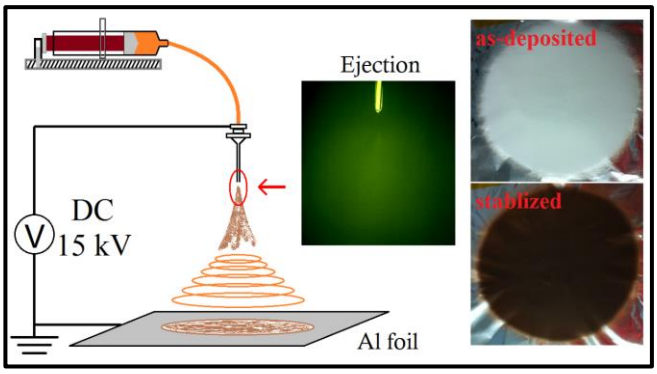

FIG.1. Left: Diagram of electro-spun PAN nanofiber membrane setup, Right: Upper: as-deposited PAN fiber before stabilization, Lower: PAN CNFs after stabilization.

In this paper, we developed a PAN nanofiber membrane and studied its filtration ability for micron-size particles. The stabilized PAN nanofibers membrane is insoluble and chemical stable in water or under a temperature of 500˚C in air [11],[12]. Besides, it is chemically inert after stabilization in an acid solution and is biocompatible to human beings, which ensures it will not cause a secondary biological hazard [13],[14]. Because of its biological compatibility, the PAN fiber has been widely used in medical prostheses, tissue template, wound dressing, drug delivery, cosmetics, as well as protective clothing [15].

Experiment

The electrospun deposition process of PAN is shown in FIG.1. PAN powder with an average molecular weight of 150,000 from Scientific Polymer Products was dissolved in *N*,*N*-dimethyformamide (DMF) solvent purchased from Fisher Scientific [16]. A homogeneous PAN solution with a concentration of 15% (weight/volume) can be achieved after a 3 hour ultrasonication (Hielscher UP400S) in air. Then, the prepared PAN solution was transferred into a 20 mL syringe (Just Fusion TM, NE-300), which connected to a metallic needle with an inner diameter of 0.495mm. The solution was then squeezed out of the needle tip using a syringe pump. The eject flow rate was set to 15 ml/h and a voltage of 15 kV was then applied between the jet needle and an Al foil (top-to-collector distance: 20 cm). The nanofiber would lie onto the substrate and the voltage was adjusted to control the deposition thickness.

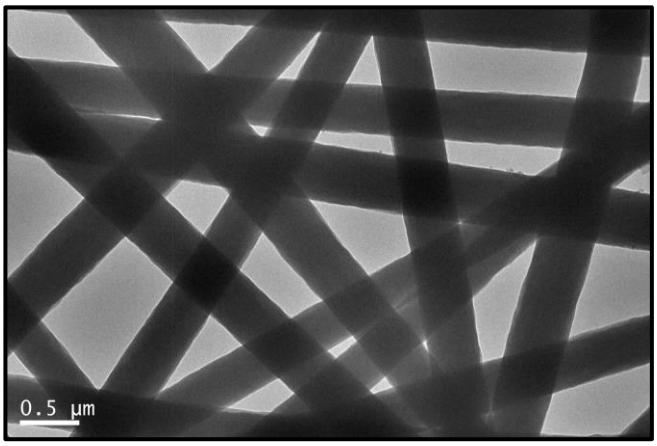

FIG.2. TEM image of stabilized PAN nanofibers. All these nanofibers show an excellent uniformity in diameter. The TEM image was acquired by FEI TEM Tecnai G2.

Three samples were then collected from the Al foil after 20 min, 40 min, and 60 min, labeled as S20, S40, and S60 respectively. The diameter of the deposited PAN effective area is ~6 cm. The TEM image of stabilized PAN nanofiber is shown on FIG.2. All the nanofibers demonstrated a uniform diameter without beads or other impurities on the outer surfaces. Then all the three samples were transferred to a furnace and annealed to remove all the residual DMF solvent. The carbonization process required two-steps: one to heat the PAN nanofiber membrane in air around 280 ºC for 30 min, the other to heat the membrane in an inert gas atmosphere (Ar/N_2) at 800 ºC for 4 hours. In the first step a ladder structure was formed; therefore, the chain scission and relaxation could be avoided during the subsequent carbonization step [17]. For the second carbonization step the higher temperature was used, which led to a formation of higher strength and high modulus carbon fibers [18].

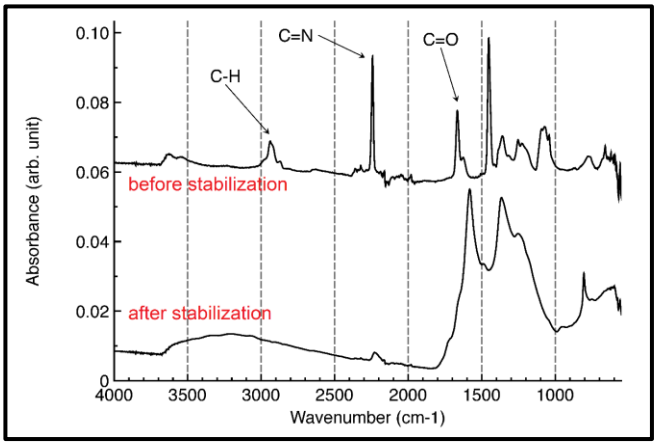

FIG.3. FTIR results of PAN nanofiber membrane before/after stabilization process. The C=N peak vanished after stabilization process, indicated that DMF had been totally removed from the PAN nanofiber membrane. The FTIR spectra was measured by Thermofisher Scientific Co. Nicolet 380.

The Fourier transform infrared (FTIR) spectra exhibited obvious peaks at 2938 cm^{-1}, 2243 cm^{-1}, 1452 cm^{-1}, 1359 cm^{-1}, and 1253 cm^{-1}, which corresponded to C-H stretching, C=N, and various aliphatic C-H groups, respectively (as shown in FIG.3). The peak at 1666 cm^{-1} is attributed to the C=O group, which originated from the residual DMF solvent [19]. The vanished peaks proved that DMF had been totally removed throughout the stabilization process. The electrospun PAN fibers before and after the

stabilization process were characterized with SEM (JEOL, JSM-700F), as shown in FIG.4. After annealing, the PAN nanofiber construction remained the same as before while its morphology became smooth. The average diameter of the PAN nanofiber was ~600 nm for as-deposited samples. Meanwhile, the average diameter shrank 50~70 nm after stabilization (count 100 fibers).

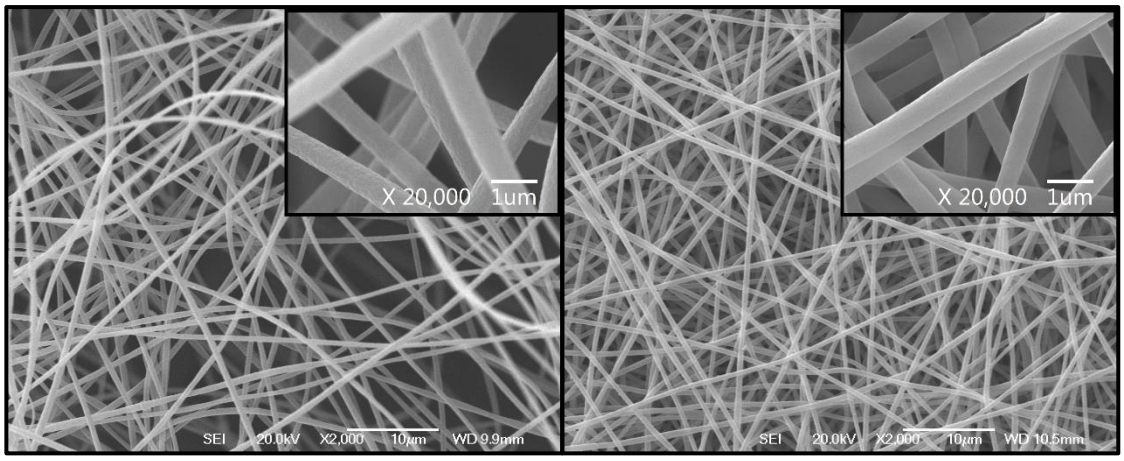

FIG.4. SEM images of Electrospun PAN nanofiber membrane (S20) before (upper figure) and after (lower figure) stabilization in ambient gas.

Experimental Analysis and Discussion

We also proposed a novel and safe method to quantitatively calculate the filtration efficiency of PAN nanofiber membrane. To simulate a near-ideal $PM_{2.5}$ filtration process, a micron-size diamond particles (MD) suspension was prepared. The diamond particles with a diameter of ~2 μm were purchased from Logitech Ltd. The MD suspension (as shown in FIG.5) was prepared at 0.2 mg/L and then sent to an ultrasonic bath for 30 mins. The reason that MD particles were used for the test is due to their proper particle diameter (~2 μm) and their insolubility in liquid. In addition, the MD particles are completely made of carbon, which is similar to the main composition of inhalable $PM_{2.5}$ particles [9]. On the other hand, micron/nano-size diamond particles have been proved to be nontoxic and biologically friendly and thus safe for the experiment operator in particle filtration [20].

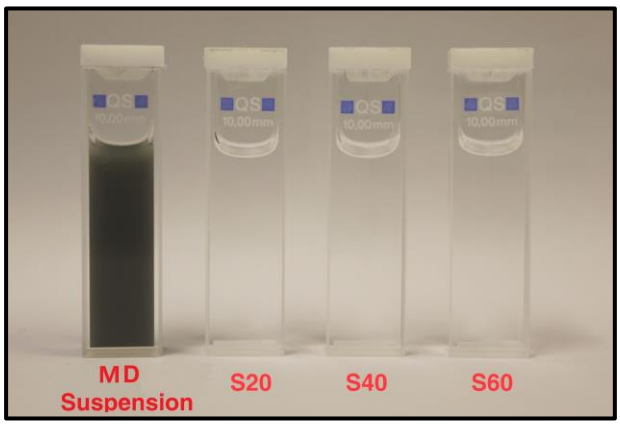

FIG.5. Photograph of MD solution after electro-spun PAN nanofiber filtration (from left to right): average 2 μm MD particles in water suspension; the suspension after filtration by: S20; S40; S60.

Afterwards, the MD suspension was suction filtrated throughout the stabilized electro-spun PAN nanofiber membrane. The stabilized PAN nanofiber membrane was fixed at the top of the flask, and the suspension after filtration could be collected, as shown in FIG.5. Comparing the MD suspension before and after filtration it is obvious that the MD suspension turned to clear through visible observation. All the PAN nanofiber membranes after filtration were characterized by SEM, as shown in FIG.6 (a)-(c). All the images were taken by SEM (JEOL, JSM-700F) with an acceleration voltage of 20.0 kV. It is obvious that no beads were found on the PAN nanofibers and MD particles were blocked on the network. In addition, the PAN nanofibers demonstrated an excellent adhesive ability on the particles because of their electrostatic force [21].

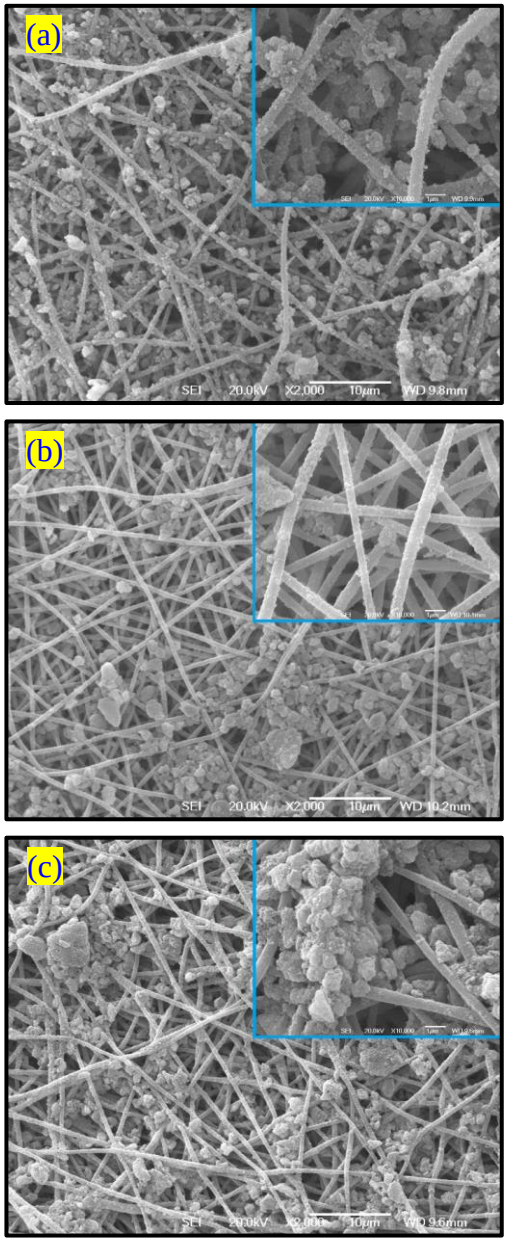

FIG.6. SEM images of electro-spun PAN nanofiber after filtration of 1 μm MD particles suspension solution: (a) S20; (b) S40; (c) S60. Main figures had a magnification: ×2,000, inset figures: ×10,000.

To determine the purification efficiency quantitatively a particle size analysis (PSA) machine (Malvern Mastersizer 2000) was used to characterize the particle size distribution in the purified liquid. Through laser diffraction analysis, it is possible to measure particle sizes between 0.02 and 2000 μm in a certain suspension liquid. The measurement used DI water with a constant amount of 20-50 micron-size particles as a reference background signal. The MD suspension and the samples after filtration were dripped into the tank (approximately 0.1~0.2 mL per test). The PSA results of the particle size distribution are shown in FIG.7, and all the data have been normalized to the same amount of 20-50 micron-size particles. It is obvious that diluted MD suspension has a significant distribution peak at ~2 μm, but it vanishes after S20, S40, and S60 membrane filtration. By integrating the corresponding area, the percentage of 1~10 μm particles can be deduced. Quantitative analysis proved that the filtration efficiency of S20, S40, and S60 were ~95%, ~97%, and ~99% respectively. A thicker membrane will lead to a better filtration efficiency, while the suction pressure and time will be increased as well. Comparing with recent report, the PAN nanofiber membrane has a better performance on filtration efficiency because of its uniform morphology, consistent diameter distribution and ordered structure in a thin layer [9].

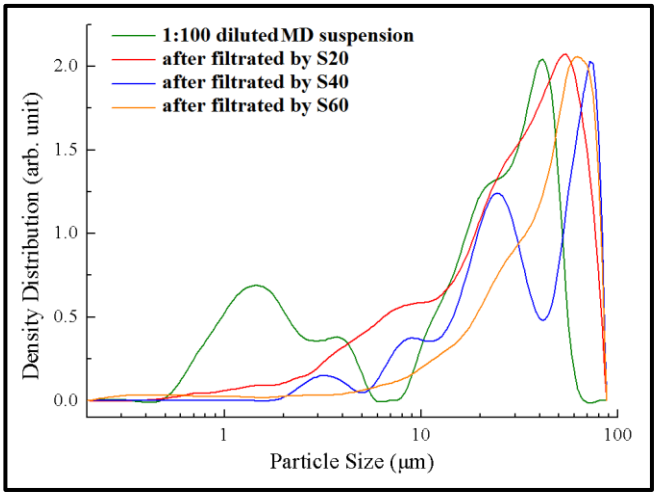

FIG.7. PSA results for MD solution before and after PAN nanofiber filtration. The amount of 20-50 μm particle distribution has been normalized to a same level in order to confirm its filtration efficiency.

To verified the chemical stability of PAN nanofiber membrane, electrochemical properties was characterized in sulfuric acid environment with Autolab 320N electrochemistry station (2M H_2SO_4 solution). The electrochemistry impedance spectroscopy (EIS) exhibited a semicircle in high-frequency with a 45° tail to low-frequency range, as shown in FIG.8. The corresponding equivalent circuit has been extracted to be a standard Warburg element as well as a constant phase element (CPE) mixing system. Deduced from the high frequency range, the diameter of the semicircle indicated that the conductance of the PAN nanofiber membrane was lower than 100 ohmic. The extremely low resistance indicates that the PAN nanofiber has been thoroughly carbonized. The cyclic voltammetry (CV) was performed with scan rate of 5 mV/s for 5 rounds. There were inconspicuous oxidization/reduction peaks on CV curves, which proved that materials were relative chemical stable in an acid solution. The PAN nanofiber membrane demonstrated a stable chemical properties in 2M sulfuric acid solution by EIS and CV measurement, which enable its future applications in strong acid and aqueous environment [19].

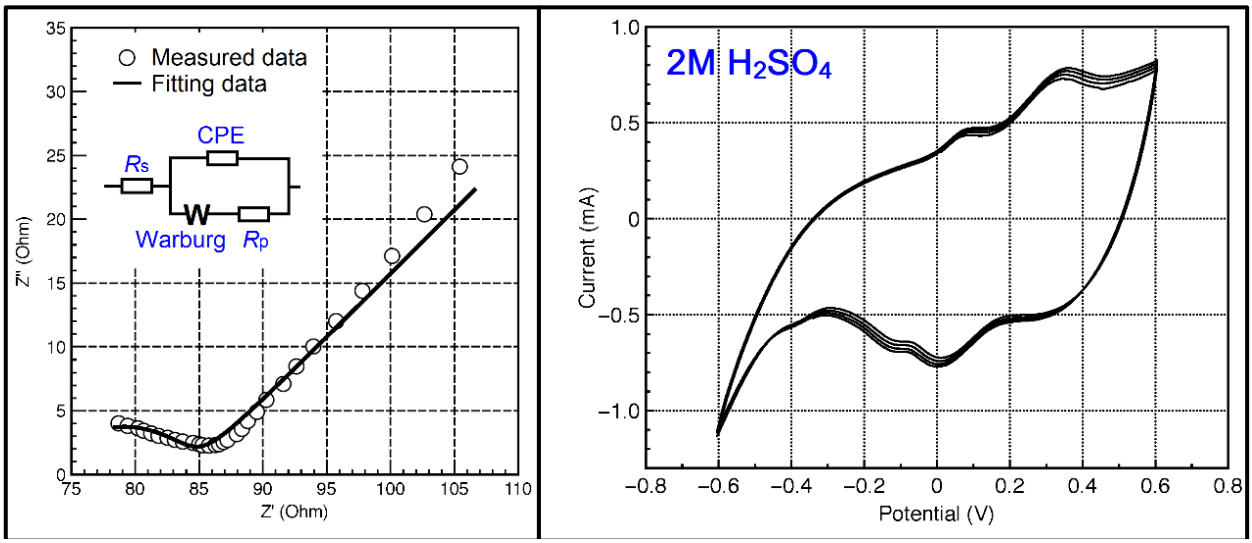

FIG.8. Electrochemical properties of PAN nanofiber membrane in acid solution. Upper: EIS spectra; Lower: Cyclic voltammetry. Electrolyte: 2M H_2SO_4.

For future investigations, a deposition on fabric materials will be a feasible approach to provide a sustain structure, and then for large area coverage applications. Besides, the PAN nanofiber membrane has an unexpected low resistance after stabilization, which enable its electrostatic adhesion ability to micron-size particles under a constant applied voltage [22].

Theoretical Analysis

To evaluate the filter performance of PAN nanofiber membrane, a theoretical model has been proposed. According to Darcy's law, the relationship of pore size and fiber size can be expressed as [23]:

$$d^2 = \frac{32D^2}{(1-c)^2 . f(c,L)} \qquad \text{Equ. 1}$$

where D is the fiber diameter, d is average pore size, c is network density and $f(c)$ is a function of c and deposition thickness L. The efficiency of filtration η is written as [24]:

$$\eta = a_1 e^{-b_1 d} = a_2 e^{-b_2 D} = \alpha e^{-\beta L^{-1}} \qquad \text{Equ.2}$$

considering deposition L is a similarly normal distribution to deposition time, the final equation can be written by:

$$\eta = \alpha e^{-\beta\sqrt{2\pi}e^{\frac{1}{2}\chi t^2}} \qquad \text{Equ.3}$$

taking η =99, 97, 95 and t =60, 40, 20 in this equation, respectively. Solving this equation, we can get α = 83.2827, β = -0.0505, and χ=0.0002. Thus the final filtration efficiency can be expressed as:

$$\eta = 83.2827 e^{-0.0505\sqrt{2\pi}e^{0.0001t^2}} \qquad \text{Equ.4}$$

The theoretical calculation proves that the particle penetration through the electrospun filters are strongly dependent with filter thickness, filter quality, filter diameter, as well as the web density. The

filtration performance of PAN nanofiber membrane was significantly improved when comparing with commercial filter, which could be attributed to the high degree of uniformity in the volume.

Summary

In this paper, we have proposed an electro-spun method to produce ultra-thin PAN membrane for micron-size particle filtration. The synthesis facilities are simple and low-cost, while the whole process is fast, environmental friendly and straightforward. We also established a novel standard and a new simulation approach to quantitatively confirm the filtration efficiency, which can be further applied in all the similar materials. The final product is ultra-thin, bio-compatible and thermal stable, which can be further attached to a fabric-cloth mask. We found that nanofiber morphology, diameter will play a critical role on its filtration performance. Future research will focus on its combination with sustain structures, as well as other advanced materials. The final goal is to apply it in an integrated system for real-time $PM_{2.5}$ filtration.

Acknowledgement

This work is supported by the Project supported by the Project supported by the National Natural Science Foundation of China (No. 11525415, 51420105003, 11327901 and 61274114); Scientific Research Starting Foundation for Returned Overseas Chinese Scholars 2015; General Financial Grant from the Chinese Postdoctoral Science Foundation (Grant No. 2015M580375); General Financial Grant from the Jiangsu Province Postdoctoral Science Foundation (Grant No. 205020500001); National Science Foundation of Jiangsu Province (Grant No. BK20160702).

References

[1] Q. Wang, China's citizens must act to save the environment, Nature 497 7448 (2013) 159.

[2] C. A. Pope III, R. T. Burnett, M. J. Thun, E. E. Calle, D. Krewski, K. Ito and G. D. Thurston, Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution, JAMA 287 9 (2002) 1132.

[3] P. Dadvand, J. Parker, M. L. Bell, M. Bonzini, M. Brauer, L. A. Darrow, U. Gehring, S. V. Glinianaia, N. Gouveia and E. Ha, Maternal exposure to particulate air pollution and tern birth weight: a multi-country evaluation of effect and heterogeneity, Environ. Health Persp. 121 3 (2013) 267.

[4] J. Wang, Y. Lei, J. Yang and G. Yan, China's air pollution control calls for sustainable strategy for the use of coal, Environ. Sci. Technol. 46 8 (2012) 4263.

[5] L. Huang, S. S. Manickam, J. R. McCutcheon, Increasing strength of electrospun nanofiber membranes for water filtration using solvent vapor, J. Membr. Sci. 436 1 (2013) 213.

[6] J. Li, F. Gao, L. Liu and Z. Zhang, Needleless electro-spun nanofibers used for filtration of small particles, eXPRESS Polymer Letter 7 8 (2013) 683.

[7] L. Jing, K. Shim, C. Y. Toe, T. Fang, C. Zhao, R. Amal, K.-N. Sun, J. H. Kim, and Y. H. Ng, Electrospun Polyacrylonitrile-Ionic Liquid Nanofibers for Superior PM2.5 Capture Capacity, ACS Appl. Mater. Interface 8 (2016) 7030.

[8] Y. Wang, G. Zhuang, A. Tang, H. Yuan, Y. Sun, S. Chen and A. Zheng, The ion chemistry and the source of PM2.5 aerosol in Beijing, Atmos. Environ. 39 21 (2005) 3771.

[9] C. Liu, P.-C. Hsu, H.-W. Lee, M. Ye, G. Zheng, N. Liu, W. Li, and Y. Cui, Transparent air filter for high-efficiency PM2.5 capture, Nat. Comm. 6 6205 (2015) 1.

[10] E. Zussman, X. Chen, W. Ding, L. Calabri, D. A. Dikin, J. P. Quintana, R. S. Ruoff, Mechanical and structural characterization of electrospun PAN-derived carbon nanofibers, carbon 43 10 (2005) 2175.

[11] S. F. Fennessey, R. J. Farris, Fabrication of aligned and molecularly oriented electrospun polyacrylonitrile nanofibers and the mechanical behavior of their twisted yarns, Polymer, 45 12 (2004) 4217.

[12] R. Luoh, and H. T. Hahn, Electrospun nanocomposite fiber mats as gas sensors, Compos. Sci. Technol. 66 14 (2006) 2436.

[13] Q. Zhang, J. Welch, H. Park, C. Wu, W. Sigmund, and J. C. Marijinissen, Improvement in nanofiber filtration by multiple thin layer of nanofiber mats, J. Aero. Sci. 41 2 (2010) 230.

[14] K. M. Yun, C. J. Hogan, Y. Matsubayashi, M. Kawabe, F. Iskandar, K. Okuyama, Nanoparticle filtration by electrospun polymer fibers, Chem. Eng. Sci. 62 (2007) 4751.

[15] Z. –M. Huang, Y. Z. Zhang, M. Kotaki, S. Ramakrishna, A Review on Polymer Nanofibers by Electrospinning and Their Applications in Nanocomposites, Composit. Sci. Tech. 63 (2003) 2223.

[16] J. Li, S. Su, L. Zhou, V. Kundrat, A. M. Abbot, F. Mushtaq, D. Ouyang, D. James, D. Roberts and H. Ye, Carbon nanowalls grown by microwave plasma enhanced chemical vapor deposition during the carbonization of polyacrylonitrile fibers, J. Appl. Phys. 113 2 (2013) 024313.

[17] T. –H. Ko, The influence of pyrolysis on physical properties and microstructure of modified PAN fibers during carbonization, J. Appl. Poly. Sci., 43 (1991) 589.

[18] Handbook of Carbon, Graphite, Diamond and Fullerenes, Edited by H. O. Pierson, William Andrew Publishing, Oxford, 1993.

[19] PhD. Thesis, Jiangling Li, Aston University, 2014.

[20] Nanodiamonds: Applications in Biology and Nanoscale Medicine, Edited by Dean Ho, Springer Publisher, New York, 2009.

[21] Electrospun Nanofibers for Energy and Environmental Applications, Edited by B. Ding and J. Yu, Springer Berlin Heidelberg, 2014.

[22] J. Li, S. Su, L. Zhou, A .M. Abbot and H. Ye, Dielectric transition of polyacrylonitrile derived carbon nanofibers, Mater. Res. Exp. 1 3 (2014) 035604.

[23] H. Goeminne, G. Van der Perre, T. Hens, and J. Van Der Planken, Formation and growth of cu3uii in a deformed matrix, Acta Metallurgica, 22 6 (1974) 725.

[24] X. W. Li, H. Y. Kong, and J. H. He, Study on highly filtration efficiency of electrospun polyvinyl alcohol micro-porous webs, Indian. J. Phys. 89 2 (2015) 175.